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### COMPLETE SPECIFICATION

#### Improvements in or relating to the Manufacture of Surgical Protheses

We, KULZER & Co. G.M.B.H., of Schillerplatz 5-7, Frankfurt a.M., Germany, formerly of Hanauer Landstrasse, 137, Frankfurt a. Main, Germany, a German Company, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

10 This invention relates to a process for the manufacture of surgical protheses, particularly dental protheses.

In general rubber is employed as starting material for the manufacture of protheses. Rubber, however, has numerous disadvantages from hygienic, cosmetic and aesthetic points of view. Rubber protheses can never be made entirely odourless and tasteless and moreover on use readily acquire the taste and smell of food. Rubber protheses are porous and have a tendency to absorb impurities. Finally rubber is non-transparent and can only be coloured with difficulty so that rubber protheses always have a lifeless and unnatural appearance.

Numerous proposals have already been made to replace rubber in the manufacture of protheses by solid polymerisation products of organic compounds, for example polystyrol, polyvinyl or polyacryl compounds. These solid artificial resins are either introduced into the mould in a comminuted or powdered condition or the so-called block method is employed, according to which casts are produced in a few standard forms from artificial resins by compression in metal moulds and these casts are then re-shaped by compression in special gypsum moulds. These processes, particularly the block methods, possess numerous disadvantages. The preliminarily moulded casts must be re-shaped in relatively costly and large dental flasks especially prepared for the purpose. In this case use must be made of the inverted embedding method to which dental mechanics are not accustomed. Since re-shaping of the cast is effected under high pressure, the said dental flasks must be filled with particularly hard and pressure-resisting gypsum of the American Alba stone type

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or the synthetic products known in the trade as "Moldano". This hard gypsum is costly and difficult to bed out. Re-shaping is effected by heating the dental flasks in costly and complicated apparatus, whereby the susceptibility to heat of the artificial resin materials must be taken into consideration by exact adjustment to prescribed temperatures. The dental flask cannot be again opened during the pressing operation so that it is impossible to ascertain whether the gypsum mould is completely filled with material. For this reason an excess of solid polymerisate is in general employed, which however increases the height of the bite in the finished protheses and makes it necessary to fit the protheses in the mouths of the patients. Most of the solid artificial resin protheses materials hitherto known are moreover susceptible to water vapour and must therefore be protected by metal foils or lacquer coatings. The working up of solid polymerisation products of organic compounds to protheses accordingly differs in all individual details from the method of working up rubber with which the dental mechanic is familiar. Special instruction is required for the working up of such polymerisation products.

According to this invention it has been found that protheses can be manufactured in the manner usually employed for working up rubber and without the occurrence of the aforesaid disadvantages from polymerised organic compounds if a plastic kneadable mass is produced by mixing a solid, comminuted, preferably powdered, polymerisate, suitable for the manufacture of protheses with a liquid monomeric or only partially polymerised compound capable of being hardened by polymerisation, if desired with the addition of known substances, and the said mass is introduced by procedures such as "ramming" or "spreading" into a mould consisting of the dental flask type obtained for example by direct impression of the part to be reproduced in gypsum and the mass is solidified in the mould by polymerisation of the said liquid material.

As starting materials all polymerisable

organic compounds may be employed, which in a monomeric or partially polymerised condition are thinly liquid to viscous and can be converted by polymerisation into a solid condition. Particularly suitable compounds are polymerisable unsaturated organic compounds, such as vinyl compounds, acryl compounds, styrol and its derivatives and polymerisation products of these compounds. Mixtures of liquid monomeric or only partially polymerised acryl compounds with solid polyacryl compounds are employed with particular advantage. Of these compounds the acrylic acid esters, for example the alkyl esters of acrylic acid or of the substituted acrylic acids, such as methacrylic acid, are preferred. It has been further found to be advisable to employ a mixed polymerisate as solid component. As liquid component use is preferably made of the monomeric or partially polymerised primary substance of the solid polymerisate, i.e. when using a solid mixed polymerisate, the mixture of the corresponding monomeric or partially polymerised compounds. Liquid and solid components differing fundamentally from one another may however also be employed. Furthermore mixtures of polymerisates may be used for the solid components.

The solid component of the mixture is with advantage employed in an extensively comminuted to powdered condition, if desired in varying sizes of grain. Before being introduced into the mould it is thoroughly mixed with the liquid component, in such proportions that the mixture assumes the properties of a plastic and kneadable, tough rubber-like paste. This mass is introduced into the mould in a suitable manner, for example by "ramming" or "spreading" preferably as soon as possible after mixing the constituents.

Gypsum moulds in two or more parts may be employed such as are usually used in the working up of rubber material. Likewise the usual dental flasks may be employed. A gypsum model of a decayed tooth provided with an opening corresponding to the cavity may be employed as mould.

The polymerisation of the liquid components may be accelerated in known manner by the addition of liquid polymerisation catalysts, such as oxygen-evolving agents, for example hydrogen peroxide or benzoyl peroxide. By adding regulators, such as turpentine oil, the polymerisation may be caused to proceed quietly. Besides these additions, artificial or natural resins, softeners, soluble colours or insoluble pigments, fillers of

the most varied kinds, cellulose derivatives, such as cellulose esters, for example cellulose tripropionate and cellulose ethers, may be added depending upon the desired effect. Solid or liquid additions may be added to the solid component or to the liquid component of the initial mixture or to both components before or during mixing or be worked into the finished mixture.

The polymerisation of the liquid component is effected by heating the filled mould to temperatures at which the formation of bubbles in the filling mass cannot take place. If necessary increased pressure is employed and this pressure may be applied in the manner customary when making rubber dentures. Owing to the peculiar tough and plastic, but non-adhesive, character of the filling mass, the latter does not bake onto the walls of the mould during polymerisation, so that it is unnecessary to line the mould with a thin coating of material adapted to prevent baking on. As a consequence thereof considerably more accurate impressions are obtained, since the space is not reduced by a lining layer. If desired however the walls of the mould may be lined in known manner with waterglass, gelatine, polyvinyl alcohol or the like substance in order to facilitate the removal of the cast from the mould.

The process of this invention possesses considerable advantages over the hitherto known methods of working up solid polymerisation products of organic compounds. One of the chief advantages is that the method of operating and the apparatus are the same as those employed for the production of rubber protheses and are familiar to the dental mechanic. The patterns may be embedded "reversed" or "normal". The filling mass may be introduced in known manner by "ramming" or "spreading". The usual gypsum moulds, dental flasks and pressing and heating devices are employed.

A further advantage of the process of this invention is that when using mould of two or more parts these can be again opened after being closed or pressed together in the usual manner, which is not possible when employing only solid polymerisation products. It is possible according to the invention to ascertain by opening the mould whether the filling mass has filled up all parts of the mould or not and in the latter case to introduce further quantities of filling material. The re-opening of the mould may be facilitated in known manner by laying sheets of cellophane or introducing other insulating agents between the individual parts of the mould.

It is also possible after opening the mould to remove excess portions of filling material which on pressing the mould parts together have penetrated between the same and thereby to avoid undesirable increases in the height of the bite of the finished prostheses.

The process according to the invention also offers important advantages in the carrying out of repairs on finished prostheses. If, for example, a crack had to be repaired in a dental plate manufactured in known manner from artificial resin, it was hitherto necessary to embed this plate in gypsum, to lay a thin sheet or plate of artificial resin on the crack and to cause the latter to unite with the plate and fill up the crack by pressing on another correspondingly shaped part. It is however not possible in this way to produce a satisfactory and permanent joint between the pressed in mass and the basic or primary mass.

When employing mixtures according to this invention such repairs can easily be effected by the method employed for repairing rubber prostheses, i.e. by cutting dove-tailed openings in the dental plate approximately vertically to the crack and starting from the latter, i.e. openings which widen out from the crack, filling these openings with a mixture of a solid polymerisable and a liquid polymerisable compound by ramming and, after superimposing another correspondingly shaped mould part, polymerising in the usual manner. In this way, exactly as when repairing rubber prostheses, owing to the dove-tailed projections of the mass rammed into the crack of the dental plate, the latter is firmly connected with the plate. In the same manner prostheses which have been manufactured in another manner from artificial materials may be permanently repaired according to the invention.

The prostheses according to this invention may be produced in any desired colour and be adjusted to any desired transparency. They are entirely odourless and tasteless, do not acquire the odour and taste of food and are not susceptible to water or to the acids and alkalis present in the mouth.

The process of this invention may be used both for the manufacture of dental prostheses or gum facings for rubber and metal prostheses (of the type known under the Registered Trade Mark Gencivex type) and also for the manufacture of surgical prostheses of other kinds, for example for the manufacture of artificial foot insertions by taking individual impressions.

The following examples serve to illus-

trate how the process of the invention may be carried into effect:

1. 60 parts by weight of a mixture of 80 parts by weight of methacrylic acid methyl ester and 20 parts by weight of acrylic acid butyl ester which has been polymerised to the point of hardening are kneaded in powder form with the addition of 0.4 parts by weight of a red pigment and 0.02 parts by weight of a white pigment together with 40 parts by weight of a mixture as aforesaid of methacrylic acid methyl ester and acrylic acid butyl ester in monomeric liquid form to a rubber-like mass. This mass is introduced by ramming into a gypsum mould, for example a di-part gypsum mould, produced in known manner. After closing the mould and pressing the mould parts together the mould is again opened and further filling material is introduced into any parts that have not been completely filled. The mould is then again closed and heated in order to polymerise the filling. This may be effected by heating the closed mould in water for half an hour at 60° C., then for half an hour at 80° C. and finally for one hour at 100° C. An alternative procedure is to heat the mould in stages in a vulcaniser or by dry heat or in oil or in glycerine and thereby to maintain the temperature, for example in the last stage, at about 115° C. by only for half an hour.

After the polymerising process is completed the mould is opened and the cast is removed in known manner and polished.

2. A mixture of 60 parts by weight of a hardened polymerised mixture is worked up in the same manner as in Example 1 with 40 parts by weight of a monomeric liquid mixture of which both the prepolymerised component and the component employed whilst still in a monomeric liquid condition consist of 10 parts of acrylic acid methyl ester, 10 parts of acrylic acid nitrile, 20 parts of vinyl acetate and 60 parts of methacrylic acid methyl ester as well as the additional substances indicated in Example 1, is worked up in the same manner as in Example 1.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the manufacture of surgical prostheses, particularly dental prostheses, from polymerised organic compounds, wherein a plastic kneadable mass is produced by mixing a solid comminuted, preferably powdered, polymerisable, suitable for the manufacture of

- protheses, with a liquid monomeric or only partially polymerised compound, capable of being hardened by polymerisation, if desired with the addition of known substances, and a mould of the dental flask type obtained, for example by direct impression in gypsum of the part to be reproduced, is filled with the plastic kneadable mass and the latter is solidified in the mould by polymerisation of the said liquid material.
2. A process as claimed in claim 1, wherein polymerisable unsaturated organic compounds, particularly acryl compounds and their polymerisation products, are employed.
3. A process as claimed in claim 1 or 2, wherein mixed polymerisates are employed.
4. A process as claimed in any one of the preceding claims, wherein the basic or primary substance of the solid polymerisate is employed as liquid component, if necessary after partial polymerisation.
5. The process for the manufacture of surgical protheses, particularly dental protheses, substantially as described with reference to the examples given.
6. Surgical protheses, particularly dental protheses, when manufactured by the process claimed in any one of the preceding claims.
7. A starting material for carrying out the process claimed in any one of the preceding claims 1 to 5, which consists of a kneadable rubber-like mixture of a solid polymerisate of an organic compound and a liquid monomeric or only partially polymerised organic compound capable of being hardened by polymerisation, if desired together with known additions.

Dated this 3rd day of March, 1937.

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